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(54) Silver halide emulsion and silver halide photographic light sensitive material

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Emulsion d'halogénure d'argent et matériau photographique à halogénure d'argent

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EP-A- 0 273 411
EP-A- 0 337 370
DE-A- 3 707 135
US-A- 4 945 037

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Description

FIELD OF THE INVENTION

This invention relates to a silver halide emulsion useful in the photographic field and to a silver halide color photographic light sensitive material applied with the above-mentioned emulsion and, particularly, to the silver halide emulsion remarkably improved in image-sharpness and pressure characteristics and to the silver halide color photographic light sensitive material applied with the above-mentioned emulsion, which is excellent in image-sharpness, pressure, color reproduction characteristics and gradation.

BACKGROUND OF THE INVENTION

Recently, in the field of silver halide color photographic light sensitive materials, the progress of super high-sensitization typified by ISO 1600 to 3200 and a small format typified by disk-films have been made and a high image-quality has therefore been required. For satisfying the requirement, a lot of studies have been made mainly on the improvements of silver halide emulsions.

For example, U.S. Patent No. 4,439,520 and Japanese Patent Publication Open to Public Inspection (hereinafter referred to as JP OPI Publication) Nos. 62-99751(1987) and 62-115435(1987) disclose the multilayered color photographic light sensitive materials having a high speed and an excellent dye-image sharpness in which the high speed layer thereof contains a tabular-grained silver halide emulsion having a grain thickness of less then 0.3 μm and an aspect ratio of not less than 8 : 1. Besides, JP OPI Publication Nos. 57-93344(1982), 54-145135(1979) and 57-151944 (1982) disclose the techniques for improving image-sharpness by making use of the diffusible DIR.

Therein the techniques of the tabular-shaped grains may be classified into those for improving an image-sharpness upon utilizing an optical effect, and the techniques of the DIR compounds may be classified into those for improving an image-sharpness upon utilizing a development effect. In particular, a light scattering produced of silver halide grains will seriously affect an image-sharpness and, as pointed out in each of the foregoing patent publications, an image-sharpness is remarkably improved when the silver halide grains are each tabular-shaped and have a thickness of less than 3 μm. Besides the above-given disclosures, there have been the disclosures of many other techniques on the above-mentioned tabular-shaped silver halide grains. For example, JP OPI Publication Nos. 58-113926(1983), 58-113927(1983) and 58-113926(1983) disclose each the emulsion grains having an aspect ratio of not less than 8.

The term, an 'aspect ratio', mentioned herein means a ratio of the thickness of a tabular-shaped silver halide grain to the diameter thereof. The term, 'the diameter of a grain', mentioned herein means the diameter of a circle having the same area as the projective area of the grain when an emulsion is observed through a microscope or an electron microscope. The term, a 'grain thickness', means the distance between the two parallel surfaces constituting a tabular-shaped silver halide grain.

The above-mentioned tabular-shaped silver halide grains are characterized in hardly monodispersing themselves as compared to any nontabular-shaped silver halide grains (which are regularly crystallized). There have been various attempts for monodispersing the tabular-shaped silver halide grains and some of the patents on the attempts have been disclosed so far.

JP OPI Publication Nos. 52-153428(1977), 55-142329(1980), 61-112142(1986) and 51-39027(1976) and French Patent No. 253,406 disclose each the techniques for monodispersing tabular-shaped silver halide grains. In every one of the techniques, the silver halide grains used therein have a low aspect ratio of less than 3 or they are the mixture of hexagonal and triangular tabular grains. Therefore, they are still not satisfactory for the monodisperse type tabular-shaped grains. As for the tabular-shaped grains uniform in both configuration and grain-size, the monodisperse type tabular-shaped grains mainly having a hexagonal configuration have been disclosed in JP OPI Publication 63-151618 (1988) equivalent to DE-A-3 707 135, 1-213637 (1989) and 2-838 (1990).

However, the tabular-shaped silver halide grains such as those mentioned above are seriously poor in pressure characteristics and it has been difficult to improve any image-sharpness without deteriorating the pressure characteristics in any conventional techniques. The term, 'pressure characteristics', has the two meanings; one meaning is that an unexposed portion is developed, that is so-called a pressure fog and the other meaning is that a photosensitive speed is lowered when making an exposure, that is so-called a pressure desensitization, each when a pressure is applied to a silver halide photographic light sensitive material. If the above-mentioned characteristics are poor, the silver halide photographic light sensitive material will have a serious defect.

It is the matter of course that the more the thickness of a tabular-shaped grain is thinner, the more the pressure characteristics are mechanically weaker and, therefore, the pressure characteristics will tend to be deteriorated. However, the pressure characteristics of the grain will be more seriously deteriorated when the grain has a higher aspect ratio even if the grain thickness remains the same. It may be interpreted that the tabular-shaped grain is liable to receive a greater moment as compared to a globular-shaped grain even if the materials of both of the grains have the same

mechanical strength. The above-mentioned pressure characteristics are varied by the distributions of the halogen compositions of silver halide grains, the conditions for a chemical sensitization and the silver halide configurations.

Generally speaking, when a chemical sensitization level is insufficient, (in other words, when a chemical ripening is made insufficiently), a pressur desensitization will be deteriorated. When a ch mical sensitization l vel is excessive, a pressure fog production will be deteriorated, though the pressure desensitization may be reduced.

When a highly iodide containing portion is made present in silver halide grains, a pressure fog production tend to be deteriorated, though the pressure fog production tend to be improved.

In the silver halide compositions, silver chloride, silver chlorobromide, silver chloroiodobromide, silver iodide or silver iodobromide may selectively be used so as to meet the purposes and applications of light sensitive materials. However, silver iodobromide may often be used in color photographic films for general use. The distribution of the grain compositions inside silver halide grains is optimized for controlling the gradations, color reproducibility and photosensitive speeds, as well as for controlling the pressure characteristics thereof. Therefore, when the color reproducibility and gradations are improved, there may often raise such an antinomic problem that the pressure characteristics may be deteriorated.

For example, when a silver halide has a higher iodine content, the silver halide will be sensitized higher. However, the light absorption wavelength region inhering in silver halide will affect the long-wavelength side and color reproducibility. Therefore, a high image-quality color film can be improved in color reproducibility by making use of silver iodobromide having a low iodine content. When silver halide is made to have a low iodine content, however, there raises such a problem that the developability (that is, the developing speed) of silver halide grains may be increased so that the gradation may be hardened. On the other hand, tabular-shaped silver halide grains will have a developing speed higher than those of the other-shaped grains even if the halogen composition thereof are the same with each other. In this case, the above-mentioned hard gradation problem may, therefore, become remarkable.

From the viewpoints of photosensitivity and pressure characteristics, it is generally desired that silver halide grains are to have a higher monodispersibility. When making use of a monodisperse type silver halide grains, however, the gradation thereof is hardened. When making use of tabular silver halide grains having a low iodine content for the purposes of improving color reproducibility and image, it cannot prepare nothing but a strikingly hard light sensitive material. Particularly in the case of color negative film which requires a wide exposure latitude and a soft gradation, the above-mentioned gradation problem is essential and it has therefore been demanded to provide an emulsion excellent in color reproduction characteristics, that is, an emulsion low in iodine content, excellent in both image-sharpness and pressure characteristics, but without spoiling the gradation thereof.

US-A-4 945 037 discloses silver halide photographic emulsions in which at least 60 per cent of the total projected area of the silver halide grains comprises tabular silver halide grains having a central portion and an outer portion. The iodide content of the central portion is from 7 mol per cent to the solution limit. The grains have two parallel twinned crystal planes. A method of making such emulsions is described.

EP-A-0 273 411 discloses a light-sensitive silver halide emulsions in which tabular grains having a diameter of 0.15 micrometres comprise least 70 per cent of the total projected area of the silver halide grains. The grains have a mean aspect ratio of more that 8.0 and at least 50 per cent (by number) of all the tabular grains have a ratio b/a of the thickness (b) to the longest spacing (a) between two or more parallel twinning planes of at least 5.

EP-A-0 337 370 discloses silver halide photographic emulsions comprising a dispersion of silver halide grains in a binder in which at least 60 per cent of the total projected area of the silver halide grains are chemically sensitized tabular silver halide grains having an aspect ration of 3 to 10 and a total silver halide content of at least 8 mol per cent. The grains have a distinct layer structure comprising at least one silver iodobromide layer in which the silver iodide content is from 15 to 45 mol per cent.

OBJECTS OF THE INVENTION

It is an object of the invention to provide a silver halide emulsion remrakably improved in image-sharpness and pressure characteristics and, at the same time, to provide a silver halide photographic light sensitive material applied with the above-mentioned emulsion.

Another object of the invention to provide a silver halide emulsion without spoiling any gradation, but excellent in image-sharpness, color reproducibility and pressure characteristics and, at the same time, to provide a silver halide photographic light sensitive material applied with the above-mentioned emulsion.

SUMMARY OF THE INVENTION

According to the present invention there is provided a silver halide emulsion comprising a dispersion medium and silver halide grains and satisfying the following requirements: (a) at least 50 per cent of the whole projective area of the silver halide grains contained in the silver halide emulsion is occupied by tabular-shaped silver halide grains having

an aspect ratio within the range 3.0 to 7.0, and (b) at least 70 per cent of the whole projective area of the silver halide grains contained in the silver halide emulsion is occupied by hexagonal tabular-shaped silver halide grains each bearing even numbers of twinned crystal faces parallel to a principal face having a maximum adjacent side ratio of 2.0 to 1.0, characterized in that said hexagonal tabular-shaped silv r halide grains hav a grain-size variation coefficient within the range of 21 to 29 percent and a thickness variation coefficient of not more than 20 percent, and when said silver halide grains contain silver iodide the relative standard deviation of silver iodide contents of individual grains is not more that 20 per cent.

There is also provided a silver halide photographic light sensitive material comprising a support carrying at least one light-sensitive silver halide emulsion layer and at least one non-light-sensitive hydrophilic colloid outer protective layer, characterized in that at least one silver halide emulsion layer contains a silver halide emulsion according to the invention.

In all the non-light sensitive hydrophilic colloidal layers each apart from the support farther than the light sensitive silver halide emulsion layer farthest from the support, the total dried layer thickness thereof is to be not thicker that 2.0 micrometres.

The silver halide photographic light sensitive material may comprise a support bearing thereon at least one each of red-sensitive silver halide emulsion layers containing each a cyan coupler, green-sensitive silver halide emulsion layers containing each a magenta coupler, and blue-sensitive silver halide emulsion layers containing each a yellow coupler. At least either one of the green-sensitive silver halide emulsion layers and/or the blue-sensitive silver halide emulsion layers contains a silver halide emulsion according to the invention.

DETAILED DESCRIPTION OF THE INVENTION

In tabular-shaped silver halide grains contained in the silver halide emulsions of the invention (hereinafter sometimes abbreviated to 'the tabular grains of the invention'), the term, an 'aspect ratio', herein means the diameter/thickness ratio of a subject grain; the term, a 'diameter of a silver halide grain', herein means the diameter of a circle having the same area with the projective area of a subject grain; and the term, a 'grain thickness', herein means a distance between two parallel faces constituting a subject tabular-shaped silver halide grain.

In the invention, the expression, 'a hexagonal tabular-shaped grain', herein means that a subject grain has a hexagonal (111) face and a maximum adjacent side ratio within the range of 1.0 to 2.0. The term, 'a maximum adjacent side ratio', herein means a ratio of the length of the shortest side of a hexagon to the length of the longest side thereof. The hexagonal tabular-shaped grains of the invention may also have rounded corners to some extent, provided, the maximum adjacent side ratio thereof is to be within the range of 1.0 to 2.0. When the corners of the hexagon is rounded to some extent, the length of a hexagonal side is to be expressed by the distance between the two points intersecting a line extended from the straight portion of a subject side and each of the lines extended from the straight portions of the adjacent sides each other.

In the hexagonal tabular-shaped grains of the invention, each of the sides thereof substantially comprises a straight line having a length of, desirably, not shorter than one half of the side length and, preferably, not shorter than four-fifths of the side length. In the invention, an adjacent side ratio is preferable to be within the range of 1.0 to 1.5.

The silver halide emulsions of the invention are generally comprised of a dispersion medium and silver halide grains. In not less than 70%, desirably not less than 80% and preferably not less than 90% of the silver halide grain projective areas, the grains are each shaped in a hexagon having an adjacent side ratio within the range of 1.0 to 2.0. And, the grains are occupied by tabular-shaped silver halide grains each having two parallel twinned-crystal faces.

The hexagonal tabular-shaped grains stated in the invention are characterized in having a plurality of (e.g., a couple of) parallel twinned-crystal faces. This fact can be confirmed by observing the cross section of the thin layer cut piece of an emulsion-coated film at a low temperature (i.e., at a liquid nitrogen temperature) through a transmission type electron microscope.

The term, 'the variation coefficient of grain sizes', stated in the invention, herein means the degrees of a grain size scattering, and it is expressed by a percentage obtained when the standard deviation of the projective areas (converted into the circular diameter) of hexagonal tabular-shaped grains of the invention having a maximum adjacent side ratio within the range of 1.0 to 2.0 is divided by the average grain size.

The term, 'the variation coefficient of grain thickness', stated in the invention, herein means the degrees of a grain thickness scattering, and it is expressed by a percentage obtained when the standard deviation of the thickness of hexagonal tabular-shaped grains of the invention having a maximum adjacent side ratio within the range of 1.0 to 2.0 is divided by the average thickness.

In at least 50% of the whole projective area of the silver halide grains of the invention, they are comprised of tabular-shaped grains having an aspect ratio within the range of 3.0 to 7.0. It is preferred that the tabular-shaped grains are to have an aspect ratio within the range of 3.0 to 7.0 in at least 70% of the whole projective area.

The aspect ratio thereof is to be within the range of 3.0 to 4.9, desirably, in at least 50% of the whole projective

area and, preferably, in at least 70% of the whole projective area.

If the aspect ratio is too high, pressure characteristics (such as a pressure desensitization and a pressure fog production) will be deteriorated, because the maximum moment is increasingly applied to silver halide grains when a pressure is applied to a light sensitiv mat rial. On th contrary, if the aspect ratio is too low, an image-sharpness will undesirably be deteriorated by a light scattering, because grains are thickened to shorten the projective diameter so as to become closer to the length scattering visible rays of light.

The above-mentioned aspect ratio has an optimum value from the viewpoints of pressure characteristics and image-sharpness. It is, therefore, the matter of course that the proportions of the grains out of the desirable aspect ratio range are preferred to be the less, the better in the distribution of silver halide grains.

At least 70% of the whole projective area of the silver halide grains contained in an emulsion is to be occupied by the silver halide grains of the invention each bearing even numbers of the twinned crystal faces parallel to the principal face formed in a hexagon having a maximum adjacent side ratio within the range of 2.0 to 1.0; and at least 90% of the whole projective area is preferably occupied by the hexagonal tabular-shaped silver halide grains such as those mentioned above.

It is also desirable that at least 70% of the whole projective area is occupied by hexagonal tabular-shaped grains having a maximum adjacent side ratio within the range of 0.1 to 1.5 and it is further preferable that at least 90% of the whole projective area is occupied by hexagonal tabular-shaped grains having a maximum adjacent side ratio within the range of 0.1 to 1.5. If the percentage of the hexagonal tabular-shaped grains is relatively low, it makes higher the percentage of the mixture of various other-shaped silver halide grains such as those having regular-crystals, triangular twinned crystals and various multiple twinned crystals.

When mixing the above-mentioned grains having the different configurations, the grains are chemically sensitized on different levels according to the configurations of the grains, because the chemical sensitization is seriously affected by the configurations, surface indexes, compositions and defects each of silver halide grains. It is, therefore, not only unable to satisfy the optimum chemical sensitization requirements because of the relation between a sensitivity and a fog production, but also unable to make the pressure characteristics satisfactory as the whole, because the grains worse in pressure fog production and excessive in chemical ripening are mixed with the grains worse in pressure desensitization and insufficient in chemical ripening. In the conditions where a large number of hexagonal tabular-shaped grains having a high maximum adjacent side ratio (i.e., triangular grains having rounded corners) are produced, the maximum adjacent side ratios of each grain are liable to be scattered, that is, a group consisting of grains each different in configurations is liable to be produced. Therefore, the chemical sensitization can hardly be optimized and the resulting emulsion is also deteriorated in pressure characteristics. It is, therefore, not desirable.

In the silver halide emulsions of the invention, pure silver bromide and silver iodobromide can preferably be used. From the viewpoint of color reproducibility aptitude, the average silver iodide content of silver iodobromide is desirably not more than 10 mol%, more desirably not more than 8 mol% and preferably not more than 6 mol%. From the viewpoint of color reproducibility aptitude, pure silver bromide having a silver iodide content of less than 0.5 mol% is preferably used. From the viewpoint of the emulsion stability, those having a slight silver iodide content is desirably used. From the overall viewpoints, the optimum silver iodide content is within the range of 0.1 to 6 mol%, desirably 0.5 to 4 mol% and preferably 1 to 3.5 mol%.

From the viewpoints of color reproducibility aptitude and gradation, the average silver iodide content is preferably within the above-mentioned range. From the viewpoint of pressure characteristics, the silver iodide contents of individual silver halide grains of an emulsion are preferable to be uniform among the grains, because a chemical sensitization is affected by the silver iodide content thereof as well as by the aforementioned grain configurations. The silver iodide contents of individual grains can be measured by making use of an XMA (standing for an X-ray microanalyzer). When defining the percentage of the standard deviation of the silver iodide contents of individual grains measured by an XMA to an average silver iodide content as a relative standard deviation, (refer to JP OPI Publication No. 60-254032/1985), such a relative standard deviation is not more than 20% and preferably not more than 15%, from the viewpoint of pressure characteristics.

In the hexagonal tabular-shaped grains of the invention, the grain sizes thereof are desirably not smaller than 0.4 μm, more desirably within the range of 0.5 to 3.0 μm and preferably within the range of 0.5 to 1.7 μm.

In the tabular-shaped grains of the invention, the average grain thickness thereof is within the range of desirably 0.05 to 0.3 Mm, more desirably 0.05 to 0.25 μm and preferably 0.05 to 0.20 μm. The grain sizes and grain thicknesses thereof can be optimized so as to make the sensitivity, image-sharpness and pressure characteristics most excellent. The optimum grain size and the optimum grain thickness may be varied by other factors exerting an influence on sensitivity, image-sharpness and pressure characteristics, (such as the thicknesses of hydrophilic colloidal layers, layer hardening degrees, chemical ripening conditions, the amounts and kinds of DIR compounds used, the ISO speeds and silver-coating weights of a subject light sensitive material) which constitute a light sensitive material. The image-sharpness is more deteriorated when an average grain size and average grain thickness are more closer to a scattering length (within the range of 0.3 μm to 0.5 μm). The thicker the grain thickness is, the better the pressure characteristics

are. Even when the grain thicknesses are the same, the higher the aspect ratio is, the more the pressure characteristics are deteriorated. The larger the grain size is, the more the sensitivity is increased, but the graininess is deteriorated. It is, therefore, preferable as same as in the cases of the conventional emulsions to select the minimum grain size so as to provid a nec ssary sensitivity.

From the viewpoint of the pressure characteristics, it is preferable as mentioned above that a grain size scattering is to be as small as possible, that is, a monodispersibility is to be as higher as possible. However, the emulsions of the invention have a problem that the gradation is hardened, because the emulsions of the invention comprise each tabular-shaped grains having a higher developing rate and low iodine-containing grains, and the gradation is accelerated to be hardened by the grain sizes are monodispersed, so that the emulsions cannot be used. For the reason mentioned above, an optimum grain size distribution is selected out of the range within which the pressure characteristics and gradation can both be compatible. The optimum grain size variation coefficient is to be within the range of 21 to 29% and the hexagonal tabular-shaped grains of the invention have the variation coefficient within the above-specified range that is preferably between 21% to 26%. When the variation coefficient is too large, a chemical sensitization aptitude becomes unsatisfactory and the pressure characteristics are deteriorated by the above-mentioned presumptive reasons. When the variation coefficient is less than 21%, the gradation is unfavorably hardened, but the pressure characteristics become better. From this fact, an antinomic requirement is raised for the variation coefficient. On the silver halide grains of the invention, that is, on the hexagonally configurated tabular-shaped silver halide grains each having an aspect ratio within the range of 3.0 to 7.0 in at least 50% of the whole projective area and a maximum adjacent side ratio within the range of 1.0 to 2.0 in at least 70% of the whole projective area, the present inventors have discovered through their studies that the pressure characteristics are improved as mentioned above and the excellent pressure characteristics can be displayed up to the region where the grain size variation coefficient is relatively larger. In other words, an excellent gradation can be displayed without spoiling any pressure characteristics within the variation coefficient range of 21 to 29%. The above-mentioned facts indicate that the optimum chemical sensitization is seriously affected more by the configuration scattering than by the grain size scattering and that a satisfactorily uniform chemical sensitization can be performed among the grains by making the grain configurations uniform, even if there are slight grain size scattering. In the case of a polydisperse type emulsion having a variation coefficient of not less than 30%, the pressure characteristics are seriously deteriorated even if the emulsion comprises hexagonal tabular-shaped grains having an aspect ratio within the range of 3.0 to 7.0, because the chemical sensitization is not uniformly made.

As described above, the optimum thickness of the silver halide grains applicable to the invention is selected so as to balance the pressure characteristics with the image-sharpness. Even when an average grain thickness is the same, the smaller the grain thickness scattering is, the better. In other words, it may be considered that, even if the grains have a preferable average grain thickness from the viewpoints of pressure characteristics and image-sharpness, some parts of the too thick grains produce a light scattering and an image-sharpness deterioration and some parts of too thin grains produce a pressure fog and a pressure desensitization, so that these grains produce the defects of an emulsion. The grain thickness distribution, that is the grain thickness variation coefficient, is expressed by a percentage of the standard deviation of individual grain thickness to the average thickness thereof. On the hexagonal tabular-shaped grains of the invention, the thickness variation coefficient thereof is to be not more than 20% and preferably not more than 15%.

The emulsions of the invention are useful when they are used in various types of light sensitive materials. The emulsions of the invention are remarkably effective particularly when they are used in a silver halide photographic light sensitive material comprising a support bearing thereon at least one of light-sensitive silver halide emulsion layers and at least one of non-light sensitive hydrophilic colloidal layers and containing the silver halide emulsion of the invention in at least one of the light-sensitive silver halide emulsion layers and, further, having not thicker than 2.0 μm of the total dried thickness of the whole non-light sensitive hydrophilic colloidal layer apart from the support farther than the light sensitive silver halide emulsion layer apart farthest from the support. The above-mentioned effects may be presumably displayed because the hydrophilic colloidal layer is made present as the outermost layer of the light sensitive material (hereinafter referred to as a protective layer) so as to play a role of protecting the silver halide emulsion layers from both of a pressure desensitization and a pressure fog production, and because the thinner the protective layer is in a light sensitive material, the worse the pressure characteristics are and the pressure characteristics of an emulsion may remarkably reflect on the characteristics of the light sensitive material.

When the protective layer of a light sensitive material is made thicker, the pressure characteristics are improved. However, the image-sharpness is deteriorated in the silver halide emulsion layers coated underneath the protective layer (i.e., close to the support side). Therefore, a thinner protective layer is preferable for making higher the image-quality of a light sensitive material. The silver halide emulsions of the invention excellent in pressure characteristics are useful because the effects thereof can be displayed particularly when they are used in a light sensitive material having such a thinner protective layer as mentioned above and an excellent image-sharpness. The image-sharpness of a light sensitive material having a thin protective layer are not so much deteriorated by the presence of a protective layer and, therefore, the light scattering of silver halide grains becomes dominant. Also regarding the image-sharpness,

the effects of the tabular-shaped silver halide grains of the invention can remarkably be displayed particularly in a light sensitive material having such a thin protective layer as mentioned above..

The thickness of a protective layer means the total dried layer thicknesses of the whole non-light sensitive hydrophilic colloidal layer apart from a support farther than the silver halide emulsion layer apart farthest from the support. The thickness thereof can be measured by cutting a light sensitive material into pieces by making use of a microtome and then by measuring the cut pieces through an optical or electron microscope. The pressure characteristic and image-sharpness effects of the emulsions of the invention can be remarkably displayed in a light sensitive material provided with a thin protective layer having a layer thickness of not more than 2.0 μm and particularly not more than 1.5 μm.

The effects of the invention can be displayed in a light sensitive material provided with the above-mentioned thin protective layer and the invention is useful in a variety of light sensitive materials such as a monochromatic light sensitive material, a color reversal film and a color negative film and, the invention is particularly useful in a multilayered color light sensitive material. To be more concrete, it is particularly useful for making the image-sharpness and pressure characteristics excellent to use the tabular-shaped silver halide emulsions of the invention in the green-sensitive and/or blue-sensitive silver halide emulsions of a silver halide color photographic light sensitive material comprising a support bearing thereon at least one each of red-sensitive silver halide emulsion layers containing cyan color developing couplers, green-sensitive silver halide emulsion layers containing magenta color developing couplers and blue-sensitive silver halide emulsion layers containing yellow color developing couplers. The above-mentioned usefulness may be presumed because the blue-sensitive and green-sensitive layers are provided relatively far from the support that is provided closer to a protective layer so that the layers are liable to be affected by a pressure and the image-sharpness is liable to be affected by a light scattering in the silver halide emulsion layer provided closer to the support.

When making use of the silver halide emulsions of the invention in the blue-sensitive and/or green-sensitive layers, each of the color-sensitive layers may be comprised of a single silver halide emulsion layer or may be comprised of a plurality of layers each having the different speeds. When the layer containing the silver halide emulsion of the invention is comprised of a plurality of layers, the effects can be displayed when at least one of the component layers contains the silver halide emulsion of the invention. It is, however, preferable to contain the silver halide emulsion of the invention in two or more of the component layers.

In the invention, the hexagonal tabular-shaped grains may be comprised of any one of silver bromide, silver iodobromide, silver chlorobromide and silver chloroiodobromide and, among them, silver bromide and silver iodobromide are preferably used. Silver iodide may preferably be contained in an amount within the foregoing range. The crystal structures thereof are allowed to have a uniform structure, the compositions heterogeneous between the inside and the outside or a layered structure. It is also preferable to contain reduction-sensitization silver nuclei in the grains. It can readily be judged whether the reduction-sensitization silver nuclei are contained in the grains or not when making an exposure, internally developing in an ordinary method and then making out an H-D curve, because the reversal image of an internal fog made present therein can be observed.

In the invention, the emulsions may be of the core/shell type. The core/shell type emulsion mentioned herein means an emulsion comprising the grains each having at least an inner part (a core) and at least one outer layer (a shell), such as the double layer structured grains given in JP OPI Publication No. 61-148442/1986 and the multilayer structured grains given in JP OPI Publication No. 61-245151/1986. For example, the core/shell type emulsions may be comprised of the grains having a high iodine-containing phase, that is, a silver iodobromide or silver chloroiodobromide phase having a silver iodide content of not less than 10 mol%, desirably not less than 20 mol% and preferably not less than 25 mol%.

When preparing the silver halide emulsion of the invention, it is allowed to apply an ordinary single-jet method, double-jet method or controlled double-jet method, provided the requirements for the invention can be satisfied. Among these methods, a controlled double-jet method is particularly desirable from the viewpoint that a pH and a pAg can readily be controlled.

In the controlled double-jet method, iodine ions can usually be supplied either from an aqueous alkaline iodide solution or from the mixture of the above-mentioned aqueous solution and an aqueous solution of other alkali halides. Iodine ions may more desirably be supplied in a method in which silver iodide is supplied in the form of a solid as mentioned in JP OPI Publication No. 1-323215/1989.

According to the above-mentioned method, the materials for growing the crystals can be supplied in a triple-jet method of making use of an aqueous ammoniacal silver salt or an aqueous solution of a water-soluble silver salt, an aqueous alkaline bromide solution and a suspension containing silver iodide grains. The pH and pAg thereof can be controlled in the same manner as in an ordinary controlled double-jet method. According to the above-mentioned method, a high iodine containing phase can effectively and uniformly be formed, and a silver halide emulsion excellent in image-sharpness and pressure characteristics, which is objective of the invention, can effectively be prepared by making combination use of the silver halide emulsion of the invention. Besides, for preparing a silver halide emulsion having the same uniformity as above-mentioned, it is useful to use a method for growing silver iodobromide grains on

seed grains in an Ostwald ripening treatment, such as the method described in JP OPI Publication No. 1-183417/1989.

When preparing a silver halide emulsion in the invention, a variety of the means applicable to the field of the art can be used. For example, it is allowed to use the techniques such as a technique for doping various kinds of heavy metal salts and th complexes thereof into silver halide grains, a desalting technique (for removing dissolv d residuals) and a technique for chemical sensitization, a physical ripening or a spectral sensitization.

In an emulsion, the silver halide grains may be of the core/shell types having various structures. The silver halide emulsions are also allowed to contain an azole or other various compounds for the purposes of preventing a fog production or stabilizing the photographic characteristics in the courses of carrying out the emulsion preparation steps, preserving the emulsion or processing the development thereof.

The above-mentioned emulsions are further allowed to contain various kinds of binders such as gelatin as a dispersion medium.

When forming an emulsion layer, a gelatin layer hardener may be used.

Particularly when forming an emulsion layer, a silver halide emulsion is further allowed to contain, besides the above, a variety of well-known surfactants with the various purposes of serving as a coating aid or of preventing an staticity, improving a slidability, making an dispersive emulsification, preventing an adhesion and improving photographic characteristics (such as a development acceleration, a layer hardening and a sensitization).

When applying an emulsion prepared in the invention to a color light sensitive material, it is allowed to use the techniques and materials applicable to light sensitive materials; for example, cyan, magenta and yellow couplers are contained, in combination, in red-sensitive, green-sensitive and blue-sensitive silver halide emulsion layers, respectively. In this case, the couplers are desirable to have a hydrophobic group that is so-called a ballast group in the molecules thereof so that the couplers can be non-diffusible. The couplers may have either a 4-equivalency or a 2-equivalency to a silver ion. Each of the couplers is also allowed to contain a colored coupler having a color correction effect or a coupler capable of releasing a development inhibitor (that is so-called a DIR coupler) as a development is being progressed. Further, the couplers may also be those producing a colorless product upon coupling reaction.

As for the yellow couplers, any well-known closed-chain ketomethylene type couplers can be used. Among these couplers, a benzoyl acetanilide type and pivaloyl acetanilide type compounds may advantageously be used. The typical examples of the yellow color-developing couplers applicable thereto include those given in U.S. Patent Nos. 2,875,057, 3,265,506, 3,408,194, 3,551,155, 3,582,322, 3,725,072 and 3,891,445; West German Patent No. 1,547,868; and West German Patent (OLS) Publication Nos. 2,213,461, 2,219,917, 2,261,361, 2,414,006 and 2,263,875.

As for the magenta color developing couplers, a pyrazolone type compound, an indazolone type compound and a cyanoacetyl compound can be used. Among the compounds, the pyrazolone type compounds are particularly advantageous. The typical examples of the magenta color developing couplers applicable thereto include those given in U.S. Patent Nos. 2,600,788, 2,983,608, 3,062,653, 3,127,269, 3,314,476, 3,419,391, 3,519,429, 3,558,319, 3,582,322, 3,615,506, 3,834,908 and 3,891,445; West German Patent No. 1,810,464; West German Patent (OLS) Publication Nos. 2,468,865, 2,417,945, 2,418,959 and 2,424,467; and JP Examined Publication No. 40-6031/1965.

As for the cyan color developing couplers, a phenol type compound and a naphthol type compound can be used. The typical examples thereof include those given in U.S. Patent Nos. 2,369,929, 2,434,272, 2,474,293, 2,521,908, 2,895,826, 3,034,892, 3,311,476, 3,458,315, 3,476,563, 3,583,971, 3,591,383 and 3,767,411; West German Patent (OLS) Publication Nos. 2,414,830 and 2,454,329; and JP OPI Publication No. 48-59838/1973.

As for the colored couplers, it is allowed to use those given in, for example, U.S. Patent nos. 3,476,560, 2,521,908 and 3,034,892; JP Examined Publication Nos. 44-2016/1969, 38-22335/1963, 42-11304/1967 and 44-32461/1969; JP Application Nos. 49-98469/1974 and 50-118029/1975; and West German Patent (OLS) Publication No. 2,418,959.

As for the DIR couplers, it is allowed to use those given in, for example, U.S. Patent Nos. 3,227,554, 3,617,291, 3,701,783, 3,790,384 and 3,632,345; West German Patent (OLS) Publication Nos. 2,414,006, 2,454,301 and 2,454,329; British Patent No. 953,454; and JP Application No. 50-146570/1975.

A light sensitive material is also allowed to contain, besides the above-mentioned DIR compounds, a compound capable of releasing a development inhibitor as a development is being progressed. The compounds applicable thereto include those given in, for example, U.S. Patent Nos. 3,297,445 and 3,379,529; and West German Patent (OLS) Publication No. 2,417,914. Besides the above, it is further allowed to use the couplers given in, for example, JP OPI Publication Nos. 55-85549/1980, 57-94752/1982, 56-65134/1981, 56-135841/1981, 54-130716/1979, 56-133734/1981 and 56-135841/1981; U.S. Patent No. 4,310,618; British Patent No. 2,083,640; and Research Disclosure Nos. 18360(1979), 14850(1980), 19033(1980), 19146(1980), 20525(1981) and 21728(1982).

The above-given couplers may be contained in one and the same layer, independently or in combination, and one and the same compound may also be contained in two or more layers.

The coupler is introduced into a silver halide emulsion layer in such a well-known method as mentioned in U.S. Patent No. 2,322,027. For example, the coupler is dissolved in an alkyl phthalic acid ester (such as dibutyl phthalate and dioctyl phthalate), a phosphoric acid ester (such as diphenyl phosphate, triphenyl phosphate, tricresyl phosphate and dioctylbutyl phosphate) a citric acid ester (such as acetyltributyl citrate), a benzoic acid ester (such as octyl ben-

zoate) and an alkylamide (such as dimethyllauryl amide) or an organic solvent having a boiling point within the range of about 30°C to 150°C including, for example, a lower alkyl acetate such as ethyl acetate and butyl acetate, ethyl propionate, secondary butyl alcohol, methylisobutyl ketone, β-ethoxyethyl alkylene acetate and methyl cellosolve acetate, and the resulting solution is then dispersed in a hydrophilic colloid. It is also allowed to mix the above-given high boiling organic solvent with a low boiling organic solvent.

When the coupler has an acid group such as those of carboxylic acid or sulfonic acid,.the coupler may be introduced in the form of an aqueous alkaline solution into a hydrophilic colloid.

Generally, a silver halide emulsion layer may be added with these couplers in an amount within the range of, desirably, $2x10^{-3}$ mols to $5x10^{-1}$ mols and, preferably, $1x10^{-2}$ mols to $5x10^{-1}$ mols per mol of silver.

As for the color-fog inhibitors, a hydroquinone derivative and so forth may be used. As for the supports for forming a light sensitive material, they include those made of baryta paper, polyethylene-coated paper, synthetic polypropylene paper, glass plate, cellulose acetate, cellulose nitrate, polyvinyl acetal and polypropylene, including, for example, a polyester film such as those made of polyethylene terephthalate, and a polystyrene film. The above-mentioned supports may be suitably selected so as to meet the application purposes of light sensitive materials and the support may be sublayered if required.

After exposing a light sensitive material to light, it is developed in any well-known methods having usually been applied.

The light sensitive materials used therein the emulsions of the invention can be fit for various uses including, for example, a variety of application such as general black-and-white photography, X-ray photography, color photography, infra-red photography, microphotography, a silver dye bleaching treatment, reversal photography and a diffusion transfer process.

When applying to a multilayered color light sensitive material, it is allowed to apply to various layer structures such as a regular layer structure, an inverted layer structure and so forth, of which have been well-known in the field of the art.

For making a high speed and a high image quality compatible, various inventions have been made on the order of layer arrangements. These techniques are desirable to be combined. The inventions made on the order of layer arrangements are disclosed in, for example, U.S. Patent Nos. 4,184,876, 4,129,446 and 4,186,016; British Patent No. 1,560,955; U.S. Patent Nos. 4,186,011, 4,267,264, 4,173,479, 4,157,917 and 4,165,236; British Patent No. 2,138,962; JP OPI Publication No. 59-177552/1984; British Patent No. 2,137,372; and JP OPI Publication Nos. 59-180556/1984 and 59-204038/1984.

It is allowed particularly to make a non-light sensitive layer present among two or more emulsion layers each having the same color sensitive speed.

The speeds may also be improved by providing a reflective layer containing fine-grained silver halide grains underneath a high speed layer including particularly a high-speed blue sensitive layer. This technique is detailed in, for example, JP OPI Publication No. 59-160135/1984.

Generally, the multilayered color photographic light sensitive materials containing the emulsions of the invention contain each a cyan forming coupler in the red-sensitive emulsion layer, a magenta forming coupler in the green-sensitive emulsion layer and a yellow forming coupler in the blue-sensitive emulsion layer thereof, respectively. It is allowed to have other different combinations if occasion demands. For example, it is also allowed to combine some infrared-sensitive layers for making a pseudocolor photography or a semiconductive laser exposure.

As disclosed in U.S. Patent No. 3,497,350 and JP OPI Publication No. 59-214853/1984, it is further allowed to use such a method that a color sensitivity and a color-image forming coupler of an emulsion layer are suitably combined together and the emulsion layer is arranged to the position farthest from a support.

The emulsions of the invention are useful for multilayered type color photographic light sensitive materials. In this case, the light sensitive materials of the invention generally have each ar least one of red-sensitive silver halide emulsion layers, one of green-sensitive silver halide emulsion layers and one of blue-sensitive silver halide emulsion layers. It is desirable that each of the same color-sensitive layers thereof is to have not less than two emulsion layers each having the different color-sensitivities. It is preferable that each of the layers is to have a three-layer structure and also that a method for improving the graininess is to be used. The above-mentioned techniques are described in, for example, British Patent No. 923,045 and JP Examined Publication No. 49-15495/1974.

EXAMPLES

Now, the examples of the invention will be detailed below. It is, however, to be understood that the invention shall not be limited thereto.

EXAMPLE-1

(Preparation of a seed emulsion)

There prepared 0.6215 mols of a hexagonal tabular-shaped emulsion in the following manner.

<Solution A>	
Ossein gelatin	4.26 g
Distilled water	1700 ml
An aqueous 10% ethanol solution, containing sodium polyisopropylene-polyethyleneoxy-disuccinate	0.4 ml
KBr	1.9 g
10% H_2SO_4	10.2 ml
<Solution B>	
An aqueous 1.255N $AgNO_3$ solution	497 ml
<Solution C>	
KBr	84.6 g
KI	7.5 g
Distilled water to make	604 ml
<Solution D>	
An aqueous 1.75N KBr solution	An amount to control the following silver potential

Solutions B and C of 9.08 ml each were added into Solution A at 35°C by making use of the mixing stirrer detailed in JP Examined Publication No. 58-58288/1983 and 58-58289/1983 in a double-jet precipitation method by taking 2 minutes, so that the nuclei were produced.

After stopping the above-mentioned addition of Solutions B and C, the temperature of Solution A was raised up to 60°C by taking 30 minutes and Solutions B and C were each added again in a flow rate of 19.5 ml/min. in a double-jet precipitation method by taking 25 minutes. In the course of adding the solutions again, the silver potential was controlled to be +6 mV with Solution D (wherein the silver potential was measured at the silver ion selection electrode while serving a saturated silver-silver chloride electrode as the reference electrode.) After completing the addition of the solutions, the pH was kept at 6 with a 3% KOH solution and an aqueous solution containing 21.3 g of ossein gelatin was added, so that seed emulsion EM-0 was prepared. The resulting seed emulsion EM-0 was proved to be the hexagonal tabular-shaped grains having the maximum adjacent side ratio within the range of 1.0 to 2.0 in not less than 90% of the whole projective area of the silver halide grains and also proved through an electron microscopic observation to be that the tabular-shaped grains had an average grain thickness of 0.07 μm and an average grain size (converted into an average circular diameter) of 0.5 μm. Seed grain EM-0 contained 0.6215 mols in 4612 ml thereof.

(Preparation of a tabular-shaped emulsion of the Invention)

A tabular-shaped silver iodobromide emulsion EM-1 containing 2.46 mol% of AgI was prepared by making use of 4 kinds of the following solutions.

<Solution A>	
Seed emulsion EM-0	0.6215 mols (in 4612 ml)
<Solution B>	
An aqueous 3.50N $AgNO_3$ solution	1467 ml
<Solution C>	
KBr	599 g
KI	17.0 g
Add distilled water to make	1467 ml

(continued)

<Solution D>	
An aqueous 1.75N KBr solution	An amount to control the following silver pot ntial

The whole amount of Solutions B and C were added into Solution A at 60°C by making use of the mixing stirrer detailed in JP Examined Publication No. 58-58288/1983 and 58-58289/1983 in a double-jet precipitation method at a flow rate of 15.45 ml/min. by taking 14 minutes, so that the addition and the growth were carried out.

In the course mentioned above, the silver potential was controlled to be +28.0 mV by making use of Solution D.

After completing the addition, a washing treatment was carried out in an ordinary manner in a precipitation method (in which phenyl carbamoyl type gelatin was used) so as to remove the excessive salts. After that, an aqueous gelatin solution containing 47.57 g of ossein gelatin was added thereto and was then so stirred as to be dispersed again.

The resulting emulsion EM-1 contained 5.756 mols of silver halide in 2445 ml thereof and the pH and pAg thereof were controlled to be 5.8 and 8.06 at 40°C, respectively.

The configurations of about 3000 grains of EM-1 were analyzed by observing and measuring them through an electron microscope. The results thereof are shown in Table-1. In EM-1, the proportion of the grains having an aspect ratio within the range of 3.0 to 7.0 was proved to be 81.1%. In this emulsion, 50% of the whole projective area of the silver halide grains was occupied by the grains having an aspect ratio of not less than 4.34, and 70% of the whole projective area thereof was occupied by the tabular-shaped grains having an aspect ratio of not less than 3.86. The whole silver halide grain projective area of 93%, that was not less than 90% thereof, were also proved to be occupied by the hexagonal tabular-shaped grains having a maximum adjacent side ratio within the range of 1.0 to 2.0. Further, in the hexagonal tabular-shaped grains, the average grain size was 0.92 μ (converted into the average circle diameter thereof); the grain size distribution thereof was 21.8% in terms of the variation coefficient; the average grain thickness was 0.218 μm; and the thickness variation coefficient was 15%.

The results of the emulsion analyses

Emulsion	Em-1	EM-2
Aspect ratio of grains in 50% of the projective area	≥4.34	≥4.07
Aspect ratio of grains in 70% of the projective area	≥3.86	≥3.33
Grain proportion within an aspect ratio of 3.0~7.0	81.1%	76%
Hexagonal tabular grain proportion within a maximum adjacent side ratio of 1.0~2.0	93%	94%
Average grain size of the hexagonal tabular grains (converted into the average circle diameter)	0.92μm	0.62μm
Grain size variation coefficient of the hexagonal tabular grains	21.8%	24.2%
Average grain thickness of the hexagonal tabular grains	0.218μm	0.163μm
Grain thickness variation coefficient of the hexagonal tabular grains	15%	9%

EXAMPLE-2

(Preparation of a tabular-shaped emulsion of the Invention)

Tabular-shaped silver iodobromide emulsion EM-2 of the invention containing 3.18 mol% of AgI was prepared by making use of the 4 kinds of the following solutions.

<Solution A>	
Seed emulsion EM-0	1.464 mols (in 10868 ml)
<Solution B>	
An aqueous 3.50N $AgNO_3$ solution	994 ml
<Solution C>	
KBr	406 g
KI	11.5 g
Add distilled water to make	994 ml

(continued)

<Solution D>	
An aqueous 1.75N KBr solution	An amount to control the following silver potential

The whole amount of Solutions B and C were added into Solution A at 60°C by making use of the mixing stirrer detailed in JP Examined Publication No. 58-58288/1983 and 58-58289/1983 in a double-jet precipitation method at a flow rate of 15.6 ml/min. by taking 54.52 minutes, so that the addition and the growth were carried out.

In the course mentioned above, the silver potential was controlled to be +38.0 mV by making use of Solution D.

After completing the addition, a washing treatment was carried out in an ordinary manner in a precipitation method (in which phenyl carbamoyl type gelatin was used) so as to remove the excessive salts. After that, an aqueous gelatin solution containing 29.3 g of ossein gelatin was added thereto and was then so stirred as to be dispersed again.

The resulting EM-2 contained 4.94 mols of silver halide in 2660 ml thereof. The pH and pAg of the emulsion solution were controlled to be 5.8 and 8.06 at 40°C, respectively. The configurations of about 3000 grains of EM-2 were analyzed by observing and measuring them through an electron microscope. The results thereof are shown in Table-1. In EM-2, the proportion of the grains having an aspect ratio within the range of 3.0 to 7.0 was proved to be 76%. In this emulsion, 50% of the whole projective area of the silver halide grains was occupied by the grains having an aspect ratio of not less than 4.07, and 70% of the whole projective area thereof was occupied by the tabular-shaped grains having an aspect ratio of not less than 3.33. The whole silver halide grain projective area of 94%, that was not less than 90% thereof, was also proved to be occupied by the hexagonal tabular-shaped grains having a maximum adjacent side ratio within the range of 1.0 to 2.0. Further, in the hexagonal tabular-shaped grains, the average grain size was 0.62 μ (converted into the average circle diameter thereof); the grain size distribution thereof was 24.2% in terms of the variation coefficient; the average grain thickness was 0.163 μm; and the thickness variation coefficient was 9%.

EXAMPLE-3

For the purpose of comparing the effects of the variation coefficients and the aspect ratios, the emulsions EM-3 through EM-15 each having the different variation coefficients and aspect ratios were each prepared in the same manner as in the emulsion EM-1 prepared in Example-1. The variation coefficients and aspect ratios of these comparative emulsions were controlled by varying the amounts of the seed emulsion used and the silver potentials given in the course of the growing the seed emulsion EM-0. The silver potentials in the course of growing the seed emulsion were so controlled as to have the different values between the first half of the growth (to be in a 1/2 amount of silver added) and the last half thereof so as to meet the requirements. The optimum adding rates of Solution B and C were each selected (to be the critical growth rates) by adjusting the amount of the seed emulsion and the silver potential for the growth so as not to produce any new nucleus other than those of the seed emulsion, so that the growth was carried out. Table-2 shows the conditions for growing EM-3 through EM-15 and the configurational parameters of the silver halide grains contained each in the emulsions.

TABLE-2/a

Growing conditions				
Emulsion No.	Amount of the seed emulsion (mol)	Amount of silver grown (mol)	EAg for growth	
			First half (mv)	Latter half (mv)
EM-0	-	0.623	6	6
EM-1	0.6215	5.1345	28	28
EM-2	1.464	5.1345	38	38
EM-3	0.6215	5.1345	38	38
EM-4	0.6215	5.1345	33	33
EM-5	0.6215	5.1345	20	20
EM-6	0.6215	5.1345	10	10
EM-7	0.6215	5.1345	6	28
EM-8	0.6215	5.1345	-1	28
EM-9	1.9277	3.828	-1	-1
EM-10	0.9675	4.789	6	28

TABLE-2/a (continued)

Growing conditions				
Emulsion No.	Amount of the seed emulsion (mol)	Amount of silver grown (mol)	EAg for growth	
			First half (mv)	Latter half (mv)
EM-11	0.8287	4.927	6	28
EM-12	0.7506	5.005	20	28
EM-13	0.5649	5.191	28	38
EM-14	0.5204	5.236	38	38
EM-15	0.4277	5.333	28	38
EM-16	0.2534	4.69	28	28
EM-17	3.655	1.288	28	28
EM-18	0.984	3.959	28	28
EM-19	0.984	3.959	28	28

TABLE-2/b

Results of configuration analyses			
Emulsion No.	Average grain size D (equivalent to a circle diameter) (μm)	Side length Dcub having the same volume (μm)	Average grain thickness t (μm)
EM-0	0.50	0.2500	0.070
EM-1	0.92	0.5250	0.218
EM-2	0.62	0.3750	0.175
EM-3	0.93	0.5250	0.220
EM-4	0.93	0.5250	0.220
EM-5	0.91	0.5250	0.220
EM-6	0.92	0.5250	0.210
EM-7	0.93	0.5250	0.210
EM-8	0.94	0.5250	0.200
EM-9	0.92	0.3600	0.070
EM-10	0.92	0.4530	0.140
EM-11	0.92	0.4770	0.163
EM-12	0.92	0.4930	0.180
EM-13	0.92	0.5420	0.240
EM-14	0.92	0.5570	0.260
EM-15	0.92	0.5970	0.320
EM-16	1.49	0.6730	0.175
EM-17	0.62	0.2765	0.070
EM-18	0.62	0.4282	0.260
EM-19	0.62	0.4282	0.260

TABLE-2/c

Results of configuration analyses			
Emulsion No.	Aspect ratio of grains occupying 50% of projective area	Aspect ratio of grains occupying 70% of projective area	Grain size variation coefficient of hexagonal tabular-shaped grains
	(not less than)	(not less than)	(%)
EM-0	7.14	6.72	33.00

TABLE-2/c (continued)

Results of configuration analyses			
Emulsion No.	Aspect ratio of grains occupying 50% of projective area	Aspect ratio of grains occupying 70% of projective area	Grain size variation coefficient of hexagonal tabular-shaped grains
	(not less than)	(not less than)	(%)
EM-1	4.24	3.86	21.80
EM-2	4.07	3.33	24.20
EM-3	3.95	3.65	17.80
EM-4	4.10	3.75	18.70
EM-5	4.30	3.92	23.80
EM-6	4.44	4.05	28.40
EM-7	4.53	4.12	30.70
EM-8	4.60	4.16	34.00
EM-9	13.00	12.44	33.00
EM-10	6.57	6.05	29.00
EM-11	5.64	5.15	24.20
EM-12	5.11	4.63	23.00
EM-13	3.83	3.45	21.20
EM-14	3.50	3.15	21.20
EM-15	2.88	2.59	21.50
EM-16	8.50	8.01	26.00
EM-17	8.86	8.31	29.00
EM-18	2.39	2.30	25.00
EM-19	2.39	2.20	16.00

TABLE-2/d

Results of configuration analyses				
Emulsion No.	Thickness variation coefficient of hexagonal tabular-shaped grains (%)	Proportion of grains having an aspect ratio of 3.0 to 7.0 (%)	Hexagonal tabular grains having a maximum adjacent side ratio of 1.0 to 2.0 (%)	Remarks
EM-0	19	41	91	Seed
EM-1	15	81.1	93	Invention
EM-2	9	76	94	Invention
EM-3	13	79	92	Comparison
EM-4	12	80	91	Comparison
EM-5	14	83	92	Invention
EM-6	18	87	93	Invention
EM-7	21	83	93	Comparison
EM-8	25	78	92	Comparison
EM-9	26	9	98	Comparison
EM-10	18	72	96	Invention
EM-11	15	91	94	Invention
EM-12	13	88	93	Invention
EM-13	14	74	92	Invention
EM-14	14	71	91	Invention
EM-15	13	44	83	Comparison
EM-16	15	69	96	Comparison
EM-17	18	13	97	Comparison

TABLE-2/d (continued)

Results of configuration analyses				
Emulsion No.	Thickness variation coefficient of hexagonal tabular-shaped grains (%)	Proportion of grains having an aspect ratio of 3.0 to 7.0 (%)	Hexagonal tabular grains having a maximum adjacent side ratio of 1.0 to 2.0 (%)	Remarks
EM-18	15	12	81	Comparison
EM-19	13	4	77	Comparison

EXAMPLE-4

Silver halide photographic light sensitive materials were prepared by chemically and spectrally sensitizing the emulsions EM-1 through EM-19 (to be blue- and green-sensitive) in the ordinary methods, respectively, and the effects of the emulsions of the invention were compared to each other.

Multilayered color photographic light sensitive materials were prepared in quite the same conditions as in those given in JP Application No. 2-10971/1989, except that the other blue-sensitive emulsions were used therein. To be more concrete, Samples No.1 through No.19 were each prepared by replacing the silver halide emulsions contained in the high-speed blue-sensitive layers and the low-speed blue-sensitive layers thereof by the same amounts of chemically sensitized emulsions EM-1 through EM-19.

For each of Samples No. 1 through No. 19, the sum total of thicknesses of dried coatings on all nonsensitive hydrophilic colloidal layers which are located to be farther from the support than the photosensitive silver halide emulsion layer farthest from the support was set to 1.98 μ.

The evaluations were made in the ordinary methods on the sensitometric characteristics (of the blue-sensitive layers), pressure resistance (of the same layers) and image-sharpness (of the green-sensitive layers) each of the resulting samples. The results of the evaluations are shown in Table-3.

From the results thereof, it was proved that, when making use of the emulsions of the invention, color photographic light sensitive materials can be so prepared as to have an excellent image-sharpness, to reduce the deterioration caused by a pressure desensitization and a pressure fog production and to have an excellent gradation.

Besides the above samples, Sample No.20 was so prepared as to contain the emulsion of the invention, EM-2, in the low-speed blue-sensitive layer thereof. The same evaluations as in the above-mentioned were made on Sample No.20. The resulting Sample No.20 proves that the image-sharpness of the green-sensitive layers can be improved and that the image-sharpness of the green-sensitive layers can preferably be improved especially when making use of the emulsions of the invention in both of the high-speed and low-speed blue-sensitive layers thereof.

The image-sharpness of the red-sensitive layers can desirably be improved similar to the above-mentioned case, when making use of the emulsions of the invention in the green-sensitive layers.

TABLE-3/a

Results of characteristic evaluation						
Sample No.	Emulsion for high-speed blue-sensitive layer	Emulsion for low-speed blue-sensitive layer	Pressure desensitization on blue-sensitive layer	Pressure fog production on blue-sensitive layer	Image-sharpness of green-sensitive layer	Gradation of blue-sensitive layer
1	EM-1	EM-18	A	A	C	B
2	EM-2	EM-18	A	A	B	B
3	EM-3	EM-18	A	A	C	D
4	EM-4	EM-18	A	A	C	D
5	EM-5	EM-18	A	A	C	B
6	EM-6	EM-18	B	B	C	B
7	EM-7	EM-18	D	D	D	B
8	EM-8	EM-18	E	E	D	D
9	EM-9	EM-18	E	E	B	D
10	EM-10	EM-18	C	C	B	B

TABLE-3/a (continued)

Results of characteristic evaluation						
Sample No.	Emulsion for high-speed blue-sensitive layer	Emulsion for low-speed blue-sensitive layer	Pressure desensitization on blue-sensitive layer	Pressure fog production on blue-sensitive layer	Image-sharpness of green-sensitive layer	Gradation of blue-sensitive layer
11	EM-11	EM-18	C	B	B	B
12	EM-12	EM-18	B	B	B	C
13	EM-13	EM-18	A	A	C	B
14	EM-14	EM-18	A	A	D	B
15	EM-15	EM-18	A	A	D	C
16	EM-16	EM-18	E	D	B	B
17	EM-17	EM-18	E	E	B	C
18	EM-18	EM-18	A	B	E	B
19	EM-19	EM-18	A	A	E	E
20	EM-1	EM-2	A	A	A	A
Grade of evaluation: A = Quite excellent B = Excellent C = Good D = Insufficient E = Quite insufficient						

Claims

1. A silver halide emulsion comprising a dispersion medium and silver halide grains satisfying the following requirements:

   (a) at least 50 per cent of the whole projective area of the silver halide grains contained in the silver halides emulsion is occupied by tabular-shaped silver halide grains having an aspect ratio within the range 3.0 to 7.0, and
   (b) at least 70 per cent of the whole projective area of the silver halide grains contained in the silver halide emulsion is occupied by hexagonal tabular-shaped silver halide grains each bearing even numbers of twinned crystal faces parallel to a principal face having a maximum adjacent side ratio of 2.0 to 1.0,

   CHARACTERIZED IN THAT

   said hexagonal tabular-shaped silver halide grains have a grain-size variation coefficient within the range of 21 to 29 percent and a thickness variation coefficient of not more than 20 percent, and
   when said silver halide grains contain silver iodide the relative standard deviation of silver iodide contents of individual grains is not more that 20 per cent.

2. The silver halide emulsion according to claim 1, characterised in that the sides of said hexagonal tabular-shaped silver halide grains comprise a straight line having a length of not less than one half of the side length and the adjacent ratio is within the range of 1.0 to 1.5.

3. The silver halide emulsion according to claim 1, characterised in that the grain size of said hexagonal tabular-shaped silver halide grains is not less than 0.4 micrometres.

4. The silver halide emulsion according to claim 1, characterised in that the hexagonal tabular-shaped silver halide grains occupy at least 90 percent of a whole projective area of the silver halide grains and the tabular-shaped silver halide grains have a grain-size variation coefficient within the range of 21 to 26 percent and a thickness variation coefficient of not more than 20 percent.

5. A silver halide photographic light-sensitive material comprising a support carrying at least one light-sensitive silver halide emulsion layer and at least one non-light-sensitive hydrophilic colloid outer protective layer, characterised in that at least one light-sensitive silver halide emulsion layer contains a silver halide emulsion according to any of the claims 1 to 4.

6. A silver halide photographic light-sensitive material according to claim 5, characterised in that the support carries a blue-sensitive emulsion layer, a green-sensitive emulsion layer, and a red-sensitive emulsion layer and in that at least one out of the blue-sensitive emulsion layer and the green-sensitive emulsion layer contains the silver halide emulsion according to any of the claims 1 to 4.

7. A silver halide photographic light-sensitive material according to claim 5 or claim 6, characterised in that it carries an outer protective layer having a thickness of not less than 1.5 micrometres.

Patentansprüche

1. Silberhalogenidemulsion, umfassend ein Dispersionsmedium und Silberhalogenidkörnchen, bei der die folgenden Erfordernisse erfüllt sind:

   (a) Mindestens 50% der gesamten Projektionsfläche der in der Silberhalogenidemulsion enthaltenen Silberhalogenidkörnchen werden von tafelförmigen Silberhalogenidkörnchen eines Seitenverhältnisses im Bereich von 3,0 bis 7,0 eingenommen und

   (b) mindestens 70 Gew.-% der gesamten Projektionsfläche der in der Silberhalogenidemulsion enthaltenen Silberhalogenidkörnchen werden von hexagonalen, tafelförmigen Silberhalogenidkörnchen mit jeweils einer geraden Zahl von Zwillingskristallflächen parallel zu einer Hauptfläche mit einem maximalen Nachbarschaftsseitenverhältnis von 2,0 bis 1,0 eingenommen,

   dadurch gekennzeichnet, daß

   die hexagonalen, tafelförmigen Silberhalogenidkörnchen einen Korngrößenabweichungskoeffizienten im Bereich von 21-29% und einen Dickeabweichungskoeffizienten von nicht mehr als 20% aufweisen, und

   wenn die Silberhalogenidkörnchen Silberiodid enthalten, die relative Standardabweichung des Silberiodidgehalts der einzelnen Körnchen nicht mehr als 20% beträgt.

2. Silberhalogenidemulsion nach Anspruch 1, dadurch gekennzeichnet, daß die Seiten der hexagonalen, tafelförmigen Silberhalogenidkörnchen eine Gerade einer Länge von nicht weniger als der Hälfte der Seitenlänge umfassen und das Nachbarschaftsverhältnis im Bereich von 1,0 bis 1,5 liegt.

3. Silberhalogenidemulsion nach Anspruch 1, dadurch gekennzeichnet, daß die Korngröße der hexagonalen, tafelförmigen Silberhalogenidkörnchen nicht weniger als 0,4 µm beträgt.

4. Silberhalogenidemulsion nach Anspruch 1, dadurch gekennzeichnet, daß die hexagonalen, tafelförmigen Silberhalogenidkörnchen mindestens 90% der gesamten Projektionsfläche der Silberhalogenidkörnchen einnehmen und die tafelförmigen Silberhalogenidkörnchen einen Korngrößenabweichungskoeffizienten im Bereich von 21-26% und einen Dickeabweichungskoeffizienten von nicht mehr als 20% aufweisen.

5. Lichtempfindliches photographisches Silberhalogenid-Aufzeichnungsmaterial mit einem Schichtträger, auf den mindestens eine lichtempfindliche Silberhalogenidemulsionsschicht und mindestens eine nichtlichtempfindliche, hydrophile äußere Kolloidschutzschicht aufgetragen sind, dadurch gekennzeichnet, daß mindestens eine lichtempfindliche Silberhalogenidemulsionsschicht eine Silberhalogenidemulsion nach einem der Ansprüche 1 bis 4 enthält.

6. Lichtempfindliches photographisches Silberhalogenid-Aufzeichnungsmaterial nach Anspruch 5, dadurch gekennzeichnet, daß auf den Schichtträger eine blauempfindliche Emulsionsschicht, eine grünempfindliche Emulsionsschicht und eine rotempfindliche Emulsionsschicht aufgetragen sind und daß mindestens eine Schicht der blauempfindlichen Emulsionsschicht und der grünempfindlichen Emulsionsschicht die Silberhalogenidemulsion nach

einem der Ansprüche 1 bis 4 enthält.

7. Lichtempfindliches photographisches Silberhalogenid-Aufzeichnungsmaterial nach Anspruch 5 oder 6, dadurch gekennzeichnet, daß es eine äußere Schutzschicht einer Dicke von nicht weniger als 1,5 µm aufweist.

Revendications

1. Une émulsion d'halogénure d'argent comprenant un milieu de dispersion et des grains d'halogénure d'argcnt satisfaisants aux exigences suivantes:

(a) au moins 50% de la surface de projection totale des grains d'halogénure d'argent renfermés dans l'émulsion d'halogénure d'argent est occupée par des grains d'halogénure d'argent sous forme lamellaire ayant un rapport de dimensions compris entre 3,0 et 7,0, et
(b) au moins 70% de la surface en projection totale des grains d'halogénure d'argent contenus dans l'émulsion d'halogénure d'argent est occupée par des grains d'halogénure d'argent lamellaires hexagonaux, chacun portant un nombre pair de faces cristallines maclées parallèles une face principale ayant un rapport des côtés adjacents maximum de 2,0 à 1,0,

caractérisé en ce que
lesdits grains d'halogénure d'argent lamellaires hexagonaux ont un coefficient de variation de taille de grains compris entre 21 et 29% et un coefficient de variation d'épaisseur ne dépassant pas 20%, et lorsque lesdits grains d'halogénure d'argent contiennent de l'iodure d'argent, l'écart type relatif standard de la teneur en iodure d'argent de chacun des grains n'est pas supérieur à 20%.

2. Une émulsion d'halogénure d'argent selon la revendication 1, caractérisée en ce que les côtés desdits grains d'halogénure d'argent de forme lamellaire hexagonaux comprennent une ligne droite ayant une longueur ne dépassant pas la moitié de la longueur du côté et un rapport adjacent compris entre 1,0 et 1,5.

3. Une émulsion d'halogénure d'argent selon la revendication 1, caractérisée en ce que la taille des grains desdits grains d'halogénure d'argent de forme lamellaire hexagonaux ne dépasse pas 0,4 micromètres.

4. Une émulsion d'halogénure d'argent selon la revendication 1, caractérisée en ce que les grains d'halogénure d'argent lamellaires hexagonaux occupent au moins 90% d'une surface de projection totale des grains d'halogénure d'argent et que les grains d'halogénure d'argent de forme lamellaire ont un coefficient de variation de grains compris entre 21 et 26% et un coefficient de variation d'épaisseur ne dépassant pas 20%.

5. Un matériau photographique photosensible à base d'halogénure d'argent comprenant un support portant au moins une couche d'émulsion d'halogénure d'argent photosensible et au moins une couche de protection colloïdale hydrophile non photosensible extérieure, caractérisé en ce qu'au moins une couche d'émulsion d'halogénure d'argent photosensible contient une émulsion d'halogénure d'argent selon l'une quelconque des revendications 1 à 4.

6. Un matériau photosensible photographique à base d'halogénure d'argent selon la revendication 5. caractérisé en ce que le support porte une couche d'émulsion sensible au bleu, une couche d'émulsion sensible au vert et une couche d'émulsion sensible au rouge et en ce qu'au moins une des couches choisies parmi la couche d'émulsion sensible au bleu et la couche d'émulsion sensible au vert contient l'émulsion d'halogénure d'argent selon l'une quelconque des revendications 1 à 4.

7. Un matériau photosensible photographique à base d'halogénure d'argent selon l'une quelconque des revendications 5 ou 6, caractérisé en cc qu' il porte une couche protectrice extérieure d'une épaisseur au moins égale à 1,5 micromètres.